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INVESTIGATION OF ULTRASONIC AND THERMAL EFFECTS' INFLUENCE ON THE SIZE DISTRIBUTION OF CARBON NANOADMIXTURES*

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ABSTRACT

Results of detailed investigation of ultrasound and heat treatment of astralenes in aqueous solutions are presented. It is shown that such treatment does not lead to the required dispersion of carbon nanoadmixture: average particle size varies in the range 0.4...0.6 μm . Volumetric content of particles with a size less than 100 nm does not exceed 15% and 5% for ultrasonic and heat treatment, respectively.

Keywords: nanoparticles, dispersion, homogenization, ultrasound, heat treatment

Most of the current nanotechnology applications in the industry of building materials are based on the admixture of nanoscale powders of different nature (synthesized oxides, CNT, etc.). During production phase, the ultrasonic processing is often used for the purpose of homogenization.

So far, only a small number of researchers have chosen to focus on the interconnection between parameters of treatment process and size distribution of the powders. Most notably, Urhanova et al. [1] have proposed the heat treatment (consisted of heating the carrier medium to the 60 °C) for the homogenization of fullerene nanoadmixture; it should be noted however that such method was theoretically proved to be efficient in our early work also [2]. Chikova et al. [3] also have expressed the feasibility of the heat treatment. Furthermore, it was shown [2] that the forces (Bjerknes, Bernoulli and others) arising during ultrasound processing lead (in general) not only to the dispersion, but also to the coagulation of dispersed phase; average decrease of the aggregates' size is taking place in some localized areas only.

It's worth to mention that in the scientific literature there are almost none of experimental data concerning the ultrasonic-homogenized disperse systems containing nanoscale modifiers. We have investigated the absorbency of colloidal solutions with astralenes [2] and derived the relations between optical density and ultrasonic treatment duration. Analysis of the mentioned relations had shown that the rate of change of carrier medium's (glycerol solution) optical density is above the one for the solutions with astralenes. Moreover, it's quite hard to evaluate the size distribution on the base of data obtained in such experiments.

It was shown in some research works [4, 5] that by means of ultrasonic treatment it is impossible to produce the aggregates with size as small as particles of the original manufactured

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powder. As it follows from the data presented in [6] and [7], the combined methods of physical treatment (in which ultrasonic homogenization is only a part) are far more effective.

From the theoretical point of view [2] it's preferable to perform thermal treatment. This is due to the fact that equilibrium between sedimentation and diffusion can easily be reached at high temperature. The later facilitates the homogenization of the particles' volumetric concentration and also eases the dispersion of aggregates. Thus, it's worth to perform the additional theoretical and experimental surveys concerning the problem of combined ultrasonic-heat treatment.

According to the Shchukin-Rehbinder criterion [8], for spontaneous dispersion the surface tension at the interface layer must not exceed the value

$$\sigma_{12} \leq \gamma \frac{kT}{r^2}, \quad (1)$$

where σ_{12} - surface tension at the «liquid - solid»; γ - constant ($\gamma = 10 \dots 15$); r - radius of the particle; k - Boltzmann's constant, T - temperature.

For $r \in I(10; 1000)$ nm and $\sigma_{12} \in I(0, 4; 4 \cdot 10^{-4})$ mN/m the value of σ_{12} depends on the individual properties of contacting media. The surface tension of the medium σ_i can be represented by the planar model with unbalanced links of energy $u_{1,i}$. If the number of such links is $N_{s,i}$, then

$$\sigma_i = N_{s,i} u_{1,i}. \quad (2)$$

For the planar model

$$N_{s,i} = N_{o,i} / S_o = a_{o,i} \rho_i / m_{a,i} = a_{o,i} / V_{m,i}; \quad (3)$$

$$u_{1,i} = U_{c,i} / N_a \eta_i, \quad (4)$$

where $a_{o,i}$ - height of the molecular (atomic) layer; $V_{m,i}$ - molar volume; $U_{c,i}$ - sublimation energy; η_i - coordination number; N_a - Avogadro's number.

Thus,

$$\sigma_i = \frac{(U_{c,i} - RT) a_{o,i}}{\eta_i V_{m,i}}. \quad (5)$$

If the shape of the surface is a sphere, we will have

$$\sigma_i = \frac{1}{6} \frac{(U_{c,i} - RT)}{\eta_i V_{m,i}} \left[D - \frac{(D - 2a_{o,i})^3}{D^2} \right]. \quad (6)$$

and after replacement $D = \kappa a_{o,i}$ we get

$$\sigma_i = \frac{1}{3} \frac{(U_{c,i} - RT)}{\eta_i V_{m,i}} a_{o,i} \left[3 - 2 \frac{(3\kappa - 2)}{\kappa^2} \right]. \quad (7)$$

In case of $\kappa \gg 2$ the value $a_{o,i} \left[3 - 2 \frac{(3\kappa - 2)}{\kappa^2} \right] \approx 3a_{o,i}$, and surface tension of large spherical particles is equal to

$$\sigma_{\infty,i} = \frac{(U_{c,i} - RT) a_{o,i}}{\eta_i V_{m,i}}. \quad (8)$$

If we apply our arguments on the phase boundary, then creation σ_{12} is the process of forming a new substance, which has individual parameters: U_c , η , V_m and a_o . The same conclusion follows when writing the Young's law in the form:

$$\gamma \frac{kT}{r^2} = \sigma_{23} - \sigma_{13} \cos \theta, \quad (9)$$

where σ_{23} - surface tension at the "solid - gas"; σ_{13} - the same as "liquid - gas"; θ - wetting contact angle.

Considering the small value of $\gamma kT/r^2$ it is clear that when $\theta \rightarrow 180^\circ$ the condition

$$\frac{\sigma_{23}}{\sigma_{13} \cos \theta} \rightarrow 1$$

is not met, and at $\theta \rightarrow 0^\circ$ it is met only when

$$\frac{\sigma_{23}}{\sigma_{13}} \rightarrow 1.$$

The above is realized only in the formation at the interface compound, which is not very different in properties from the liquid phase, in particular the magnitude of surface tension.

From the presented arguments it follows that the spontaneous dispersity, intensified Brownian motion, is possible only in the formation at the interface of a solvate layer of the dispersion medium (carrier medium). The latter is realized only in the lyophilic disperse systems.

The influence of ultrasonic treatment (UST) to disperse composition was carried out on aqueous systems containing astralenes [9] and sulfanol [10] – anion surfactant, rather actively adsorbed on astralenes (Fig. 1). Dispersed analysis was carried out on «Vibra-Cell VCX 750» with power of ultrasound to 500 watts. Dispersion analysis was performed with a laser analyzer «Zetatrac»; range of particle size – from 0.8 nm to 6.5 μm .

Obviously, during the treatment of the dispersed phase ultrasound act as a sound field and causes release of thermal energy, which is formed during the absorption of ultrasound (Fig. 2).

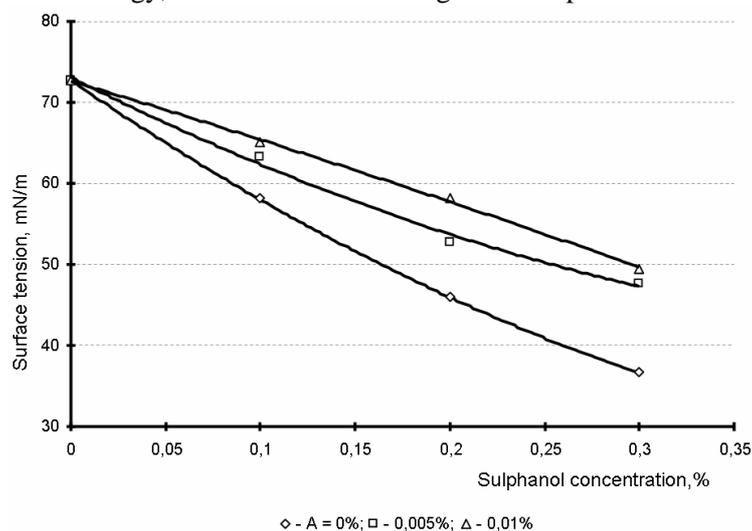


Figure 1. The dependence of surface tension on the concentration sulphanol and astralenes (denoted "A" - astralenes)

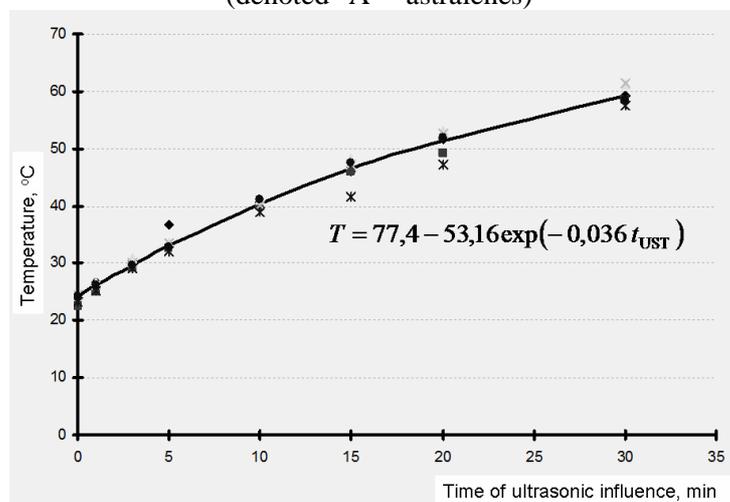


Figure 2. The dependence of solution temperature on the duration of UST

The results of the influence of ultrasound on the dispersion component of the investigated solutions are shown in Fig. 3 and 4.

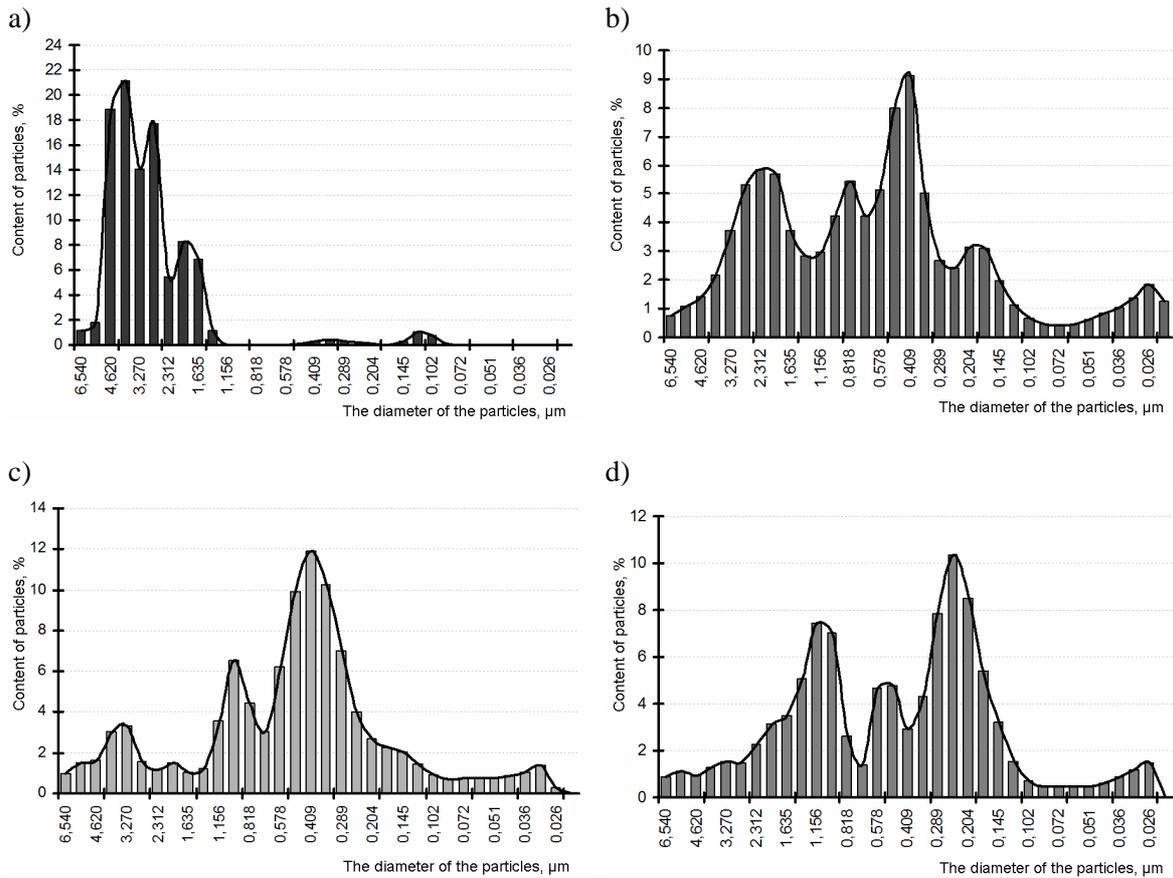


Figure 3. Dispersion component of astralenes
(composition: astralenes - 0.005%, sulfanol - 0.01%):

a) original; b) the duration of the UST is 3 min; c) the same, 15 min; d) the same, 30 min

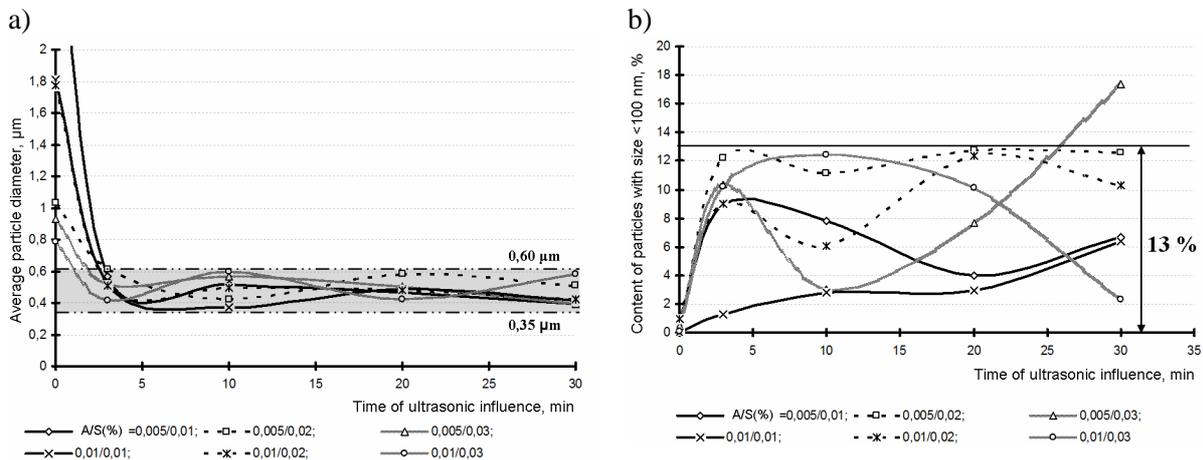


Figure 4. The dependence of the average particle size (a) and the number of particles with size <100 nm (b) the duration of UST
(notes: "A" - astralenes, "S" - sulfanol)

Analysis of Fig. 3 and 4 shows that the particle size varies rapidly in the initial 3 minutes of UST (at the size of aggregates larger than 1 μm), and with increasing size of aggregates astralenes (more than 1.8 μm) the rate of dispersity increases. At the same range of time observed an intense increase the number of particle with sizes <100 nm. Further processing does not lead to a significant change in the average diameter of aggregates astralenes (diameter ranges from 0.4...0.6 μm) and the content of particles with sizes <100 nm. The total content of particles (aggregates astralenes) with sizes <100 nm does not exceed 15%. It should be noted that the obtained kinetic dependences are

close to the periodic nature. It is consistent with the nature of ultrasound: in a working volume formed of the local area with an active dispersion and coagulation processes.

Influence of temperature on dispersion of components was carried out through research of the samples, sequentially selected from the cooling solution in natural conditions and subjected to continuous mixing (Fig. 5).

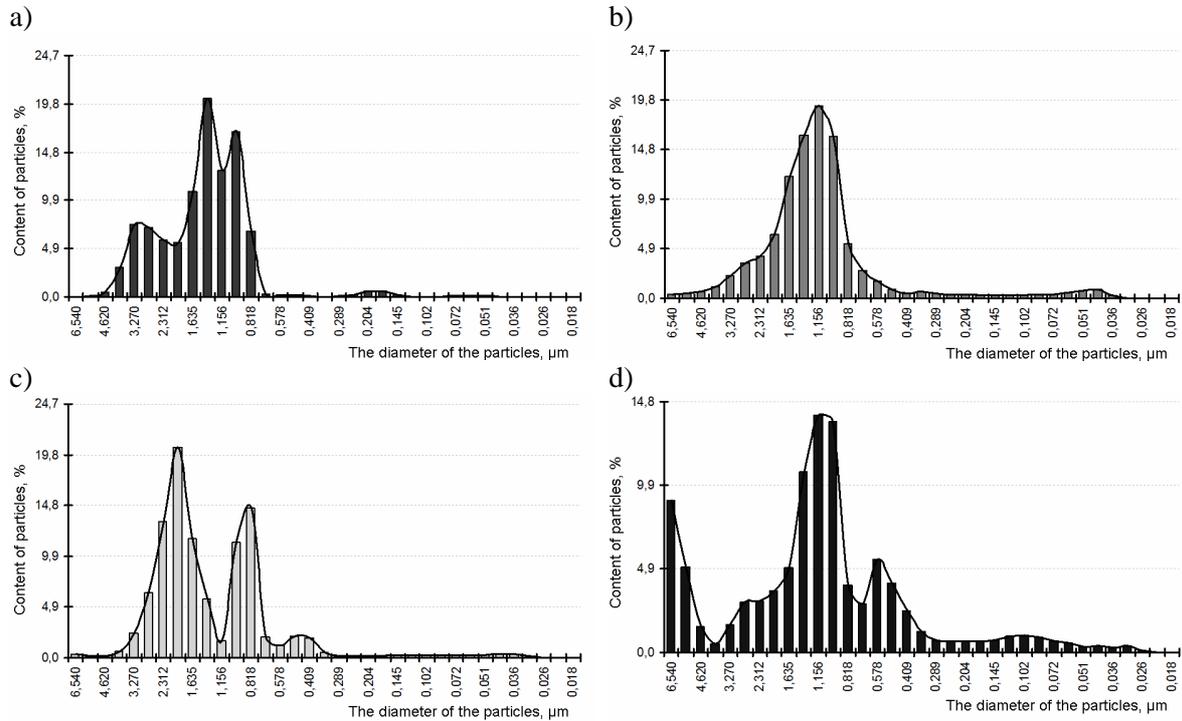


Figure 5. Dispersion component of astralenes (composition: astralenes - 0.005%, sulfanol - 0.01%): a) T = 80°C; and b) T = 60°C; c) T = 45°C; d) T = 30°C.

Experimentally determined changes in dispersity can be explained as follows. From the hypsometric distribution of Laplace [7]:

$$\frac{n_1}{n_2} = \exp\left(g \frac{(\rho_f - \rho_c) \pi}{kT} d^3 \Delta h\right) \quad (10)$$

(where n_1 and n_2 – number of particles at height h_1 and h_2 , respectively; $\Delta h = h_2 - h_1$; ρ_f – the density of the material of the particle; ρ_c – the density of the medium carrier; d - particle diameter; g – free fall acceleration; T - temperature; k – Boltzmann's constant) follows that if the particle diameter increases the difference in their number $\Delta n = n_1 - n_2$ increases

$$\frac{d(n_1/n_2)}{d(d)} = \frac{\pi}{2} d^2 \Delta h \frac{g(\rho_f - \rho_c)}{kT} \exp\left(g \frac{(\rho_f - \rho_c) \pi}{kT} d^3 \Delta h\right), \quad (11)$$

and if the temperature increases

$$\frac{d(n_1/n_2)}{d(T)} = -\frac{\pi}{6} d^3 \Delta h \frac{g(\rho_f - \rho_c)}{kT^2} \exp\left(g \frac{(\rho_f - \rho_c) \pi}{kT} d^3 \Delta h\right) \quad (12)$$

– decreases.

From the Smoluchowski theory [12]

$$\frac{n_x}{n_o} = 1 - \left(1 + \frac{8 kT}{3 \mu} n_o t\right)^{-1} \quad (13)$$

(where μ - viscosity of the carrier medium; n_0 - the total number of particles) follows that if the temperature increases then the number of collisions between particles, leading to their coalescence and an increase in the diameter of aggregates, increases:

$$\frac{d(n_x/n_o)}{d(T)} = \frac{8k}{3\mu} n_o t \left(1 + \frac{8kT}{3\mu} n_o t \right)^{-2} \quad (13)$$

Considering the influence of temperature on the adsorption of surfactants [13]

$$\Gamma = -\frac{c}{RT} \frac{d\sigma}{dc} \quad (\text{Gibbs equation}) \quad (14)$$

If the temperature increases then it will be observed sufficiently intense coagulation of particles, which will continue (the time factor in the equation of Smoluchowski) with a lower intensity with decreasing temperature (collision of the particles will be observed, but the adsorption of surfactant will prevent the formation of solid coagulation communication). Increasing adsorption of surfactant (sulphanol) with decreasing temperature, contributes to rise the number of astralenes with sizes of particle <100 nm (Fig. 6).

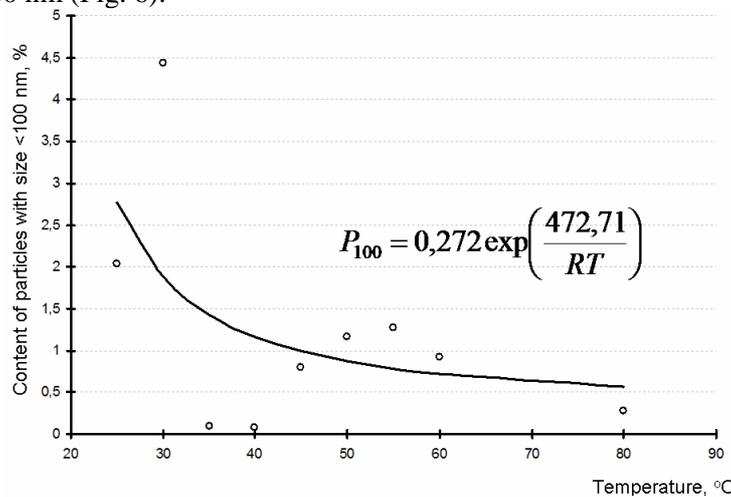


Figure 6. Dependence of the fraction astralenes with size <100 nm in the temperature

In the dispersed component of the colloidal solutions of the astralenes received by UST with duration $t = 30$ min, after 60 days of exposure under normal conditions, changes are observed (Fig. 7). Moreover, these changes depend on the conditions of sample preparation for analysis.

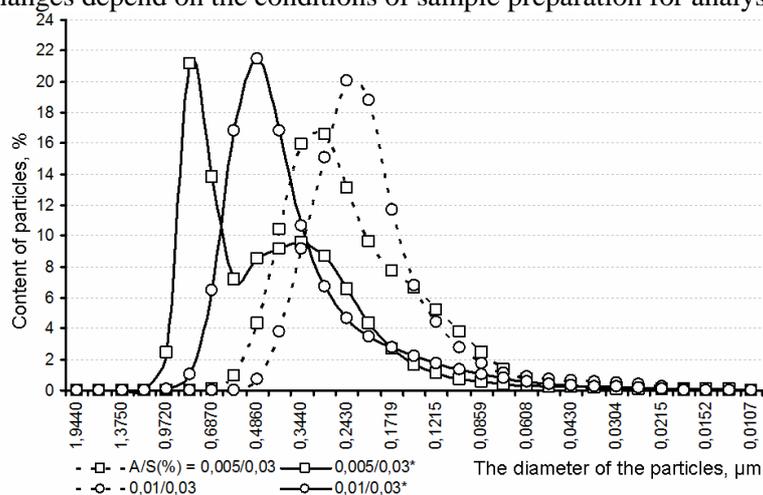


Figure 7. Dispersion component of astralenes

(notes: "A" - astralenes, "S" – sulfanol, "*" - after mixing)

When testing a sample obtained from a storage container, without pre-mixing the particle size has a mean value of 0.232 and 0.202 μm at a concentration of 0.005 and 0.01% respectively. After 1 minute of mixing (speed of 1500 rpm) large particles settled to the bottom container, distributed over

the volume, which leads to an increase in the average diameter of up to 0.435 and 0.393 microns, respectively.

The maximum particle size of less than 1 μm regardless of the surfactant concentration, when, after ultrasonic treatment to less than 15% (Fig. 3d). The content of the fraction of particles with size <100 nm has not significant changes. This change in the dispersion component of astralenes is in good agreement with previously formulated mechanism of influence of temperature and concentration of surfactants on the hysometric distribution of Laplace.

CONCLUSIONS

As it follows from the experimental investigation, ultrasonic treatment neither provides required size distribution, nor properly homogenizes the nanoscale modifiers. The greatest effect is observed only during initial stage of processing (in first three minutes), when average diameter of the aggregates decreases down to 0.4...0.6 μm (kinetic dependences are almost periodic – this is, probably, caused by the nature of ultrasound field). The total fraction of particles (aggregates of astralenes) of size less than 100 nm does not exceed 15%. Reduction of the prolonged UST effect caused by lower value of surfactants' absorption at higher temperatures (the later is due to heating during UST).

The application of the heat treatment causes two competing processes: diffusive movement of particles – which leads to the homogeneity increase of the dispersed system – and coagulation, resulting the enlargement of aggregates of particles (and therefore, intensifying their sedimentation). Moreover, at elevated temperatures, increased coagulation further decrease the adsorption of surfactant. During subsequent decrease of the temperature the coagulation continues with less intensity due to the influence of the adsorbed surfactant and the time factor. The absorption of surfactant does not induce significant increase in number of particles with size less then 100 nm (the increase is about 5%). Combined thermal-UST treatment is effective only in case of lyophilic (for modifier) carrier medium.

The presented comparison results of homogenization of nanoscale modifiers in the carrier medium show that ultrasonic treatment is more effective. However, for the application of nanotechnology in material science, using all potential inherent in nanoscale modifiers, none of the mentioned methods are perfectly suitable. Further advance in the considered direction of nanotechnology requires the development of new intensive methods of nanoscale modifiers' homogenization. The combined effect of all mixing mechanisms of the carrier medium must be taken into account, and search for new surfactants have to be carried out.

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